DETERMINATION OF CONCENTRATION OF PESTICIDE IN GROUNDWATER USING MASS BALANCE EQUATION

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Alhamdulillah…

Specially for….

Abah&Ma

Papa&Mama

My husband..Aidil

My son..Aryan

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ABSTRACT

Pesticide is a chemical used for preventing, destroying or controlling any pest. But if the uses of pesticide are much, it will harmful to life. This study will calculate the concentration of pesticides in soil column. It will involve three models which are water flow model, pesticide transport model and mass balance equation. The mass balance equation will be solved by using Crank-Nicolson finite difference method. Then the result obtained will be compared with the experimental result and analytical result. In conclusion, concentration of pesticides decreases with depth and time under steady state and unsteady state.

ABSTRAK

Racun perosak merupakan bahan kimia yang digunakan untuk mencegah, memusnahkan atau mengawal sebarang serangga. Tetapi jika digunakan secara berlebihan, ia akan membahayakan hidupan. Kajian ini akan mengira kepekatan racun perosak dalam ruangan tanah. Ia akan melibatkan tiga model iaitu model pengaliran air, model pengangkutan racun perosak dan persamaan seimbang jisim. Persamaan seimbang jisim akan diselesaikan menggunakan kaedah pembezaan terhingga Crank-Nicolson. Kemudian, keputusan yang diperoleh akan dibandingkan dengan keputusan eksperimen dan keputusan analitikal. Secara konklusi, kepekatan racun perosak berkurangan dengan kedalaman dan masa di bawah keadaan pegun dan tidak pegun.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

K	-	hydraulic conductivity
h	-	soil water pressure head
θ	-	volumetric water content
H	-	hydraulic head
z	-	soil depth
$C(\theta)$	-	differential water capacity
u	-	transpiration sink term
t	-	time
θ_S	-	water content at saturation
a	-	constant
b	-	constant
K_S	-	hydraulic conductivity at saturation
P	-	pore water interaction parameter
q	-	water flux
J_t	-	total transportation of pesticide
J_{dl}	-	liquid diffusion flux
J_{cl}	-	liquid convection flux
J_{dg}	-	gas diffusion flux
J_{cg}	-	gas convection flux

C_l	-	concentration in liquid phase
D_p	-	molecular diffusion coefficient
D_{ol}	-	molecular dispersion coefficient in liquid phase
D_M	-	hydrodynamic dispersion coefficient
V	-	velocity of water flux
λ	-	propagation coefficient
D_g	-	average gas diffusion coefficient
ε	-	voids including gas
D_{og}	-	gas diffusion coefficient in air
γ	-	coefficient
K_H	-	Henry coefficient
Φ	-	source/sink of pesticide
ρ	-	soil bulk density
C_S	-	concentration of pesticide
K_d	-	distribution coefficient
C_w	-	pesticide infiltration in water

CHAPTER 1

INTRODUCTION

1.0 Background of the study

The Food and Agriculture Organization (FAO) has defined pesticide as any substance or mixture of substances intended for preventing, destroying, or controlling any pest, including vectors of human or animal disease, unwanted species of plants or animals, causing harm during or otherwise interfering with the production, processing, storage, transport, or marketing of food, agricultural commodities, wood and wood products or animal feedstuffs, or substances that may be administered to animals for the control of insects, arachnids, or other pests in or on their bodies. The pesticide term includes chemicals or substances use as a plant growth regulator, defoliant, desiccant, or agent for thinning fruit or preventing the premature fall of fruit. It also refers to substances applied to crops to protect the commodity from degenaration during storage and transport either before or after harvest.

Most of the application of pesticides is related with agricultural industry. One of the uses of pesticides is to control organisms that are considered to be injurious. For

example, they used it to kill mosquitoes that can transmit potentially deadly diseases like West Nile virus that is transmitted by a culex mosquito, yellow fever, and malaria. Uncontrolled pests such as termites and mould can damage structures of the houses and buildings. Grocery stores and food storage facilities used pesticides to manage rodents such as mice and squirrels and insects that inhabit food such as grain. The positive impact on the use of pesticides is that it can save farmer's money by preventing crop losses to insects and other pests and farmers can get an estimated fourfold return on money they spend on pesticides. One study found that not using pesticides reduced crop yields by about 10%.

Here are some of types of pesticides and the target pest group:

Table 1.1: Types of pesticides and the target pest group

Type of pesticide	**Target pest group**
Herbicides	Plant
Algicides or Algaecides	Algae
Avicides	Birds
Bactericides	Bacteria
Fungicides	Fungi and Oomycetes
Insecticides	Insects
Miticides or Acaricides	Mites
Molluscicides	Snails
Nematicides	Nematodes
Rodenticides	Rodents
Virucides	Viruses

Even though there are lots of benefits of pesticide use there are still hazardous to the living things. The use of pesticides not only brings benefits to human but also has the bad effects to human health. One of the examples is contamination of groundwater which arises from the use of pesticides. When it contaminates the groundwater, the water needs to be cleaned before using it especially in cooking and drinking. So, high cost to clean the water is needed. Other than that, it can use to control pests and plant disease vectors by improving crop or livestock yields and controlling invasive species. To the contrary, pesticide's benefits is controlling organisms that harm other human activities and structures such as drivers view unobstructed, tree or brush or leaf hazards prevented and wooden structures protected.

Figure 1.1: Examples of pesticide use in agriculture

There are many types of pesticides use on the earth. But for this research, it focus on 2, 4-dichlorophenoxyacetic acid or usually referred to by its abbreviation, 2, 4-D and 1, 2 - dibromo 3-chloro propane. 2, 4-D is a common systemic pesticide or herbicide used in the control of broadleaf weeds. 2, 4-D is a synthetic auxin or plant hormone, and as such it is often used in laboratories for plant research and as a supplement in plant cell

culture media such as MS medium. It was a major ingredient in Agent Orange alongside its chemically similar relative, 2, 4, 5-T (2, 4, 5-trichlorophenoxyacetic acid).

Surface water and groundwater have often been studied and managed as separate resources, although they are interrelated. Groundwater is the water located beneath the earth's surface in soil pore spaces and in the fractures of rock formations while surface water seeps through the soil and becomes groundwater. Conversely, groundwater can also feed surface water sources. Groundwater is recharged from, and eventually flows to, the surface naturally; natural discharge often occurs at springs and seeps, and can form oases or wetlands. Agricultural, municipal, and industrial use groundwater which is withdrawn for by constructing and operating extraction wells. In this world, about 0.61% of the entire world's water, including oceans and permanent ice is groundwater, which is about twenty percent of the world's fresh water supply. Global groundwater storage is roughly equal to the total amount of freshwater stored in the snow and ice pack, including the north and south poles.

Concern about the environmental impact of repeated pesticide use has incited research into the environmental fate of these agents, which can emigrate from treated fields to air, other land and water bodies (Arias-Estevez *et al.*, 2008). According to the Stockholm Convention on Persistent Organic Pollutants, nine of the twelve most dangerous and persistent organic chemicals are pesticides. Pesticides can be categorized into four main substituent chemicals; herbicides (plants); fungicides (fungi); insecticides (insects) and bactericides (bacteria).

Physical, chemical and microbial factors affect the process are considered. This paper presents a model which considers all phases of transport and transformation of pesticide in soil column. Hence, the concentration of pesticide in groundwater can be predicted so that it is not contaminated and safe to use. Moreover, we can use it in

agricultural fields, domestic and industrial use if we are shortages of surface water, as in during times of drought. This makes it an important resource which can act as a natural storage.

1.1 Statement of problem

Groundwater pollution can be caused by many factors. One of the factors is the use of pesticides. Some pesticides are persistent organic pollutants and contribute to soil contamination. A number of new models have been proposed in response to recently collected field data on solute leaching patterns. BAM model by Jury *et al*. (1983) and Loague model by Loague *et al*. (1998) have been done before by analytical method and experimental result is obtained by Wagenet *et al*. (1989). Many of them have been produced as the result of research into basic physics and chemistry of salt, nitrogen, pesticide transport and transformation in agricultural soils.

This paper is done to simulate the concentration of DBCP and 2, 4-D pesticides in soil column. Before this paper is produced, the concentration of polluted groundwater is simulated based on analytical result and experimental result obtained by other researchers. Mirbagheri and Tanji (2006) had calculated the concentration of Se species in soil column. There is evidence that chemicals applied to the soil surface may be transported rapidly to groundwater passing the unsaturated soil zone (Johnson *et al.*, 1995). Toxic materials especially pesticides are being used for many purposes in the environment. These substances are adsorbed in soil environment through natural processes occurring in soil water plant relationships. Adsorption is one of the most

important factors that affects fate of pesticide in soils and determines their distribution in the soil or water environment (Kah and Brown, 2007).

The movement of pesticide residues by means of leaching through the soil profile or transport to and dispersion in the aquatic environment may cause contamination of food, result in loss of usable land and water resources to man due to contamination of groundwater supplies, or cause habitat loss to wildlife. Groundwater pollution occur when pollutants are released to the ground that can work their way down into groundwater which can contaminant plume within an aquifer. Movement of water and dispersion within the aquifer will spread the pollutant over a wider area. Its advancing boundary often called a plume edge, which can then intersect with groundwater wells or daylight into surface water such as seeps and springs, making the water supplies unsafe for humans and other wildlife.

In recent years, water and pollution movement in soil were modeled. Some of them were based on movement of soluble and washed samples in soil column. Others were the result of changing concentration of toxic materials in agricultural soils. The pesticide transport and transformation processes in soil column under transient flow condition are complex. Several complicating factors which control transport of different types of pesticides include pore water velocity, evaporation and transformation fluxes, concentration gradient and seasonal rise and fall of the water table. In general, contamination of soil and groundwater by pesticides are the result of mass flow and concentration gradient. In conclusion, studying pollutant behavior of pesticides in soil column is an important problem.

1.2 Objective of research

The objectives of this study are to

i. to obtain water flow model using Richard's equation and continuity equation
ii. to formulate the pesticide transport model
iii. to discretize the governing equation using Crank-Nicolson approximation
iv. to develop algorithm on solving the mass balance equation

1.3 Scope of the study

Scope of the study is to develop a one dimensional dynamic mathematical model to simulate two types of pesticides namely 2,4-dichlorophenoxy acetic acid and 1,2-dibromo 3-chloro propane in soil column. This work is based on the paper International Journal of Environmental, Science and Technology 6 by S. A. Mirbagheri and S. A. Hashemi Monfared (2009) entitled `Pesticide Transport and Transformation Modeling in Soil Column and Groundwater Contamination Prediction'. This is a theoretical investigation; no numerical computation is carried out.

1.4 Significance of the study

Malaysian Water Association (MWA) secretary, general Mohmad Asari Daud says groundwater is well-established as a reliable source of water overseas, with high levels of utilisation in countries such as Denmark (99%), Austria (98%), Switzerland (83%) and Thailand (80%). Meanwhile at the Groundwater Colloquium 2009, the Natural Resources and Environment Minister said:

> The wise use of groundwater resources can play a significant role in supplementing the nation's water supply requirement and reducing the impact of drought in both urban and rural environments.
>
> (Datuk Douglas Uggah Embas, 2009)

In Malaysia, there are lots of groundwater sources.

Water Resources in Malaysia
(based from JICA study 1982)

Water Resources	Quantity (billion m^3)	
Annual rainfall		990
- Surface runoff	566	
- Evapotranspiration	360	
- Groundwater recharge	**64**	
Surface artificial storage		25
Groundwater storage		**5000**

Figure 1.2: Water resources in Malaysia based on JICA study 1982.

Contamination of groundwater problems considered in this dissertation basically from the previous research that mostly are from other countries because for the time being the groundwater utilization in Malaysia is not widely used. This is because Malaysia has abundant supply of surface water from rainfall. In Malaysia, Kelantan is one state that uses groundwater more than the others. In Kelantan, 8 percent of its domestic water supply is from groundwater. Domestic water demand is increasing every year along with the demand from the agricultural and industrial sectors

For example, it was reported in The Star dated March 3, 2014 that the water levels at the Sungai Selangor dam in Kuala Kubu Baru has dropped to below 50%. In the meantime, the Energy, Green Technology and Water Ministry is mulling the idea of extracting underground water as an alternative source of water supply. Selangor Menteri Besar, Tan Sri Khalid Ibrahim had talked about it before. It has been said that we should reduce our dependence on surface water, which currently accounts for 98% of water consumed since it can be easily affected by extreme weather conditions.

Figure 1.3: Contractors digging a well in Balakong. There is water in the ground but there is the risk of contamination, cost of treatment processes and the possibility of land subsidence to consider before it can be pumped out.

In Kelantan, groundwater is extracted from the aquifers in the coastal areas in the northeastern part of the state of Kelantan. But these aquifers are exposed to saltwater intrusion especially in drought season. At that time, the pumping process will lower the groundwater level and induces the flow of the saline water into the groundwater system.

Figure 1.4: A villager drawing water from a well in Pulau Mabul, Sabah.

Hence, through this research, the model can be used as a tool to look well into the future to use pesticide in agricultural soils and consider alternative management strategies so that the groundwater is not contaminated. As groundwater represents more than 50% of the worlds drinking water supply, its contamination has received increasing attention. Amount of groundwater use in Malaysia is still small now.

1.5 Project overview

This study contains six chapters started with introductory chapter. First chapter described briefly about the research background, problem statements, objectives of the

research, scope and significance of this study. Literature review of this study will be considered in the next chapter. This chapter explained briefly about previous studies on modeling of groundwater pollution and previous studies on pesticides.

Then, the chapter three will discuss methodologies and procedure in completing this study. It will explain about water flow model, pesticide transport model, mass balance equation, Crank-Nicolson finite difference method and its boundary condition. The first and second objectives are obtained in chapter three. Next, the discretization and algorithm of the methods that are used is explained in chapter four. Results and discussion of data will be considered in the fifth chapter. In chapter five, the result is explained based on work done by Wagenet *et al*. (1989), Loague *et al*. (1998), Jury *et al*. (1983), Mirbagheri and Hashemi Monfared (2009). Finally, conclusion of this study and its recommendation for future research are discussed in chapter six.

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